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# PATENT SPECIFICATION

NO DRAWINGS

Inventors: GEOFFREY ERNEST FICKEN and JOHN DAVID KENDALL



870,753

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International Classification:—C09b. C07d. G03c.

## COMPLETE SPECIFICATION

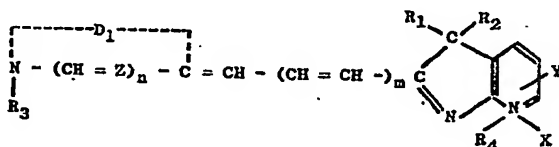
### Improvements in or relating to Methine Dyes

5 We, ILFORD LIMITED, a British Company, of 23 Roden Street, Ilford, in the County of Essex, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

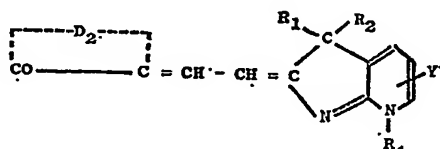
This invention relates to cyanine dyes and

particularly to cyanine dyes which contain a 3:4-diazaindene ring system. The invention further relates to photographic silver halide emulsions containing such dyes as optical sensitizers. 10

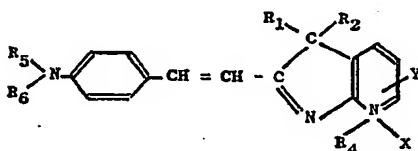
According to the present invention there are provided cyanine dyes of the general formulae I, II and III:— 15



... I



... II



... III

- 20 where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_6$  are each a lower alkyl group  $R_3$  is a lower alkyl or hydroxyalkyl group or an aralkyl group,  $R_4$  is a lower alkyl or aralkyl group,  $n$  and  $m$  are each nought or one,  $X$  is an acid radicle,  $Y$  is hydrogen or a lower alkyl substituent group,  $Z$  is  $\text{CH}$  or  $\text{N}$ ,  $D_1$  is the residue of a five-membered or six-membered heterocyclic nitrogen ring system, and  $D_2$  is the residue of a keto-methylene nucleus. The term lower alkyl used herein means an alkyl group containing 1 to 4 carbon atoms. 30

The substituents  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  are preferably methyl or ethyl groups.

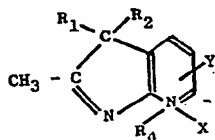
[Price 3s. 6d.]

$D_1$  may be the residue of any five-membered or six-membered heterocyclic ring system including thiazoles, oxazoles, selenazoles and their polycyclic homologues such as those of the benzene and naphthalene series; pyridine and its polycyclic homologues, such as quinoline and  $\alpha$ - and  $\beta$ -naphthoquinolines; indolenines; diazoles (e.g. 1:3:4-thiadiazole); thiazolines; diazines (e.g. pyrimidines and quinazolines). The polycyclic compounds of these series may be substituted in the carbocyclic rings with one or more groups such as alkyl, aryl, alkoxy and methylene dioxy groups, or by halogen atoms. 35 40 45

D<sub>2</sub> may be the residue of rhodanic acid (2-thio - 4 - keto - tetrahydrothiazole), oxarhodanic acid (2-thio-4-keto-tetrahydrooxazole) and the N-hydrocarbon substituted derivatives of such compounds, oxazolones, pyrazole-5-ones and thiohydantoin.

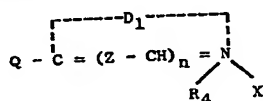
X may be any acid radicle, for example halide (chloride, bromide, iodide), sulphate, sulphamate, perchlorate or *p*-toluene sulphonate.

According to a further feature of this invention, compounds of the said general formulae are prepared by condensing a compound of the general formula IV:—



... IV

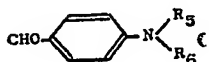
with a compound of one of the formulae V, VI and VII:—



... V



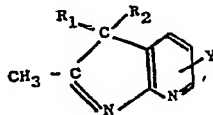
... VI



... VII

where Q is a thioether (SR), thioether vinyl (—CH=CH—SR) or acetanilidovinyl group and R is a lower alkyl group.

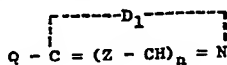
Instead of starting with a compound of general formula IV there may be used a compound of general formula IVa:—



... IVa

together with a substantially equimolecular proportion of a quaternising salt R<sub>4</sub>X.

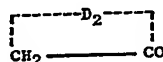
Further, when a quaternary salt such as the *p*-toluene sulphonate is used, the quaternisation may be effected by fusing an alkyl *p*-toluene sulphonate with the compound of formula IVa. The reaction may also be effected by starting with a compound of the formula IVa, a compound of the formula Va:—



... Va

and at least two molecular proportions of such a quaternising salt.

Further, there may be used, instead of a compound of formula VI a compound of formula VIa:—



... VIa

together with a substantially equimolecular proportion of a lower alkyl ortho ester.

All the foregoing condensations are facilitated by the presence of a basic condensing agent, e.g. pyridine or triethylamine.

It may be noted that where Y is an alkyl group in  $\alpha$  or  $\gamma$ -position to the nitrogen atom of the pyridine ring, there is sometimes a tendency for reaction to occur with that alkyl group to produce small proportions of by-product dyes. The dyes of the present invention are, however, readily separated by partial crystallisation or chromatography.

The dyestuffs obtained, and particularly those of formula I, are valuable sensitisers for photographic gelatino silver halide emulsions and may be used for that purpose in the manner of sensitising dyes well known *per se*.

The following is illustrative of the production of suitable intermediates of Formulae IV and IVa (temperatures throughout this specification are given in degrees Centigrade):—

1:1:2 - Trimethyl - 3:4 - diazaindene was prepared by the following procedure:—

2 - Hydrazinopyridine (Fargher and Furness, Journal of the Chemical Society, 1915, 107, 691) (115 g.), methyl isopropyl ketone (125 ml.) and dry benzene (300 ml.) were refluxed together, the water being removed as formed by azeotropic distillation. After distillation of the benzene, the residual oil was heated with zinc chloride (1 g.) at 250° until ammonia evolution ceased (2 hours). The product was distilled and the fraction boiling above 115°/6 mm. was collected and redistilled. The main fraction (b. pt. 109—132°/6 mm.) from the second distillation was extracted repeatedly with light petroleum (b. pt. 60—80°). The extracts deposited 1:1:2 - trimethyl - 3:4 - diazaindene, which was obtained as colourless needles, m. pt. 77—78°, by repeated recrystallisations from cyclohexane.

1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide.

The base (2.0 g.), methyl iodide (2.0 ml.) and acetone (10 ml.) were refluxed together for 30 minutes, when the product separated from the solution. It was obtained as colourless needles, m. pt. 218—219° (decomp.), by crystallisation from ethanol.

The following Examples will illustrate the present invention:—

## EXAMPLE 1.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2) (3 - methyl - 2 - benzothiazole) methincyanine iodide.

- 5 1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide (1.52 g.) and 2 - methylthiobenzothiazole methiodide (1.62 g.) were refluxed together in ethanol (30 ml.) containing triethylamine (1.0 ml.) for 3 hours. The dye separated from the solution on cooling, and was obtained as yellow plates, m. pt. 313—314° (decomp.) by recrystallisation from methanol.

- 15 The dye extends the sensitivity of a silver chloride photographic emulsion to 4950 Å with a maximum at 4700 Å.

## EXAMPLE 2.

(4 - Ethyl - 1:1 - dimethyl - 3:4 - diazaindene - 2)(3 - ethyl - 2 - benzothiazole) methincyanine iodide.

- 20 The dye was prepared similarly to Example 1 and was obtained as yellow prisms with a blue reflex, m. pt. 318—319° (decomp.), by crystallisation from methanol.

- 25 The dye extends the sensitivity of a silver chloride photographic emulsion to 4950 Å with a maximum at 4700 Å.

## EXAMPLE 3.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2) (1 - methyl - 2 - quinoline) methincyanine perchlorate.

- 30 The dye was prepared similarly to Example 1, was isolated by adding an aqueous solution of sodium perchlorate, and was obtained as red needles, m. pt. 250—251°, by crystallisation from a mixture of 2 - methoxyethanol and methanol.

- 35 The dye imparts a new band of sensitivity to a silver chloride photographic emulsion from 4350 Å to 5800 Å with a maximum at 5300 Å.

## EXAMPLE 4.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2) (3 - methyl - 2 - benzoxazole) trimethincyanine iodide.

- 45 1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide (0.60 g.), 2 - ω - acetanilidovinylbenzoxazole methiodide (0.84 g.) and pyridine (5.0 ml.) were refluxed together for 15 minutes. The dye, which crystallised from the solution, was obtained as blue needles, m. pt. 268—269° (decomp.), by recrystallisation from a mixture of 2-methoxy - ethanol and methanol.

- 50 The dye extends the sensitivity of a silver iodobromide photographic emulsion to 6000 Å, with maxima at 5200 and 5600 Å.

## EXAMPLE 5.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2) (1:3:3 - trimethyl - 2 - indolenine) trimethincyanine perchlorate.

- 60 The dye was prepared similarly to Example 4, was isolated by pouring the pyridine solu-

tion into an aqueous solution of sodium perchlorate, and was obtained as brown prisms with a blue reflex, m. pt. 271—272° (decomp.), by crystallisation from methanol.

65

The dye extends the sensitivity of a silver iodobromide photographic emulsion to 6250 Å with maxima at 5900 and 6200 Å.

## EXAMPLE 6.

4 - (2:4 - Dihydro - 1:1:4 - trimethyl - 3:4 - diazainden - 2 - ylidene) - ethylidene - 3 - methyl - 1 - phenylpyrazol - 5 - one.

70

Ethyl orthoformate (1.6 ml.) was added to a boiling solution of 1:1:2 - trimethyl - 3:4 - diazaindene 4-methiodide (0.76 g.) and 3 - methyl - 1 - phenylpyrazol - 5 - one (0.71 g.) in pyridine (5 ml.), and the whole refluxed for 30 minutes. The dye, which crystallised out on cooling, was recrystallised from ethanol as red plates and needles, m. pt. 251—252°.

75

The dye imparts a new band of sensitivity to a silver chloride photographic emulsion from 4600 to 5550 Å with a maximum at 5350 Å.

80

## EXAMPLE 7.

5 - (2:4 - Dihydro - 1:1:4 - trimethyl - 3:4 - diazainden - 2 - ylidene) - ethylidene - 3 - ethyl - 2 - thiothiazolid - 4 - one.

85

1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide (0.76 g.) and 5-ethoxymethylene-3 - ethyl - 2 - thio - thiazolid - 4 - one (0.54 g.) were refluxed in ethanol (10 ml.) and triethylamine (1.0 ml.) for 20 minutes. The precipitated dye was obtained as purple plates, m. pt. 257—259°, by crystallisation from a mixture of 2-methoxyethanol and methanol.

90

The dye extends the sensitivity of a silver iodobromide emulsion to 6300 Å with a maximum at 6000 Å.

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## EXAMPLE 8.

1:1 - Dimethyl - 2 - p - dimethylaminostyryl - diazaindene 4-methiodide.

100

1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide (0.60 g.) and p-dimethylaminobenzaldehyde (0.30 g.) were refluxed in pyridine (5 ml.) containing piperidine (1 drop) for 1½ hours. The dye which crystallised out on cooling was obtained as green needles, m. pt. 272—273° (decomp.), by recrystallisation from methanol.

105

The dye extends the sensitivity of a silver iodobromide emulsion to 6200 Å with a maximum at 5800 Å.

110

## EXAMPLE 9.

(4 - Ethyl - 1:1 - dimethyl - 3:4 - diazaindene - 2)(3:4 - dimethyl - 2 - thiazole) methincyanine perchlorate.

115

1:1:2 - Trimethyl - 3:4 - diazaindene 4-ethiodide (0.79 g.) and 4 - methyl - 2 - methylthiothiazole methiodide were refluxed together in ethanol (10 ml.) containing triethylamine (0.5 ml.) for 1 hour and the solution was poured into an aqueous solution of sodium perchlorate. The precipitated dye was obtained

120

as pale yellow plates, m. pt. 203—204°, by crystallisation from ethanol.

- 5 The dye imparts a new band of sensitivity to a silver chloride photographic emulsion from 4300 to 4750 Å, with a maximum at 4600 Å.

#### EXAMPLE 10.

(4 - Ethyl - 1:1 - dimethyl - 3:4 - diazaindene - 2)(3 - methyl - 4 - phenyl - 2-thiazole) methincyanine perchlorate.

- 10 The dye was prepared as in Example 9, and was obtained as yellow prisms, m. pt. 289—290° (decomp.), by crystallisation from methanol.

- 15 The dye extends the sensitivity of a silver chloride photographic emulsion to 4850 Å with a maximum at 4650 Å.

#### EXAMPLE 11.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2)(1 - methyl - 2 - quinoline) trimethincyanine iodide.

- 20 1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide (0.60 g.) and 2- $\omega$ -ethylthiovinylquinoline methiodide (0.71 g.) were refluxed together in ethanol (10 ml.) containing triethylamine (0.5 ml.) for  $\frac{1}{2}$  hour. The dye which separated from the solution was obtained as deep green plates, m. pt. 250—251° (decomp.), by crystallisation from ethanol.

- 30 The dye imparts a new band of sensitivity to a silver iodobromide photographic emulsion from 5850 to 6550 Å with a maximum at 6300 Å.

#### EXAMPLE 12.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2)(1 - methyl - 4 - quinoline) trimethincyanine iodide.

- 35 The method of Example 11 was used, the dye being obtained as blue-green needles, m. pt. 298° (decomp.), by crystallisation from methanol.

#### EXAMPLE 13.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2)(3 - methyl - 2 - benzothiazole) trimethincyanine iodide.

- 45 The method of Example 11 was used, the dye, being obtained as deep blue needles m. pt. 269—270°, by crystallisation from methanol.

- 50 The dye extends the sensitivity of a silver iodobromide photographic emulsion to 6400 Å, with a maximum at 6050 Å.

#### EXAMPLE 14.

(1:1 - Diethyl - 4 - methyl - 3:4 - diazaindene - 2)(3 - methyl - 2 - benzoxazole) trimethincyanine perchlorate.

- 55 A mixture of 1:1 - diethyl - 2 - methyl - 3:4 - diazaindene (0.66 g.) and methyl toluene-*p*-sulphonate (0.80 g.) was heated at 100° for 20 minutes. The product was refluxed in pyridine (10 ml.) with 2 -  $\omega$  - acetanilidovinyl-

benzoxazole methiodide (1.1 g.) for 1 hour. The dye was precipitated by pouring the resulting solution into aqueous sodium perchlorate solution, and was obtained as brown needles with a blue reflex, m. pt. 191°, by crystallisation from ethanol.

#### EXAMPLE 15.

(1:1 - Diethyl - 4 - methyl - 3:4 - diazaindene - 2)(3 - methyl - 2 - benzothiazole) trimethincyanine perchlorate.

The method of Example 14 was employed, the dye being obtained as blue needles, m. pt. 203—203.5°, by crystallisation from ethanol.

The dye extends the sensitivity of a silver iodobromide photographic emulsion to 6250 Å with a maximum at 6000 Å.

#### EXAMPLE 16.

(1:1 - Diethyl - 4 - methyl - 3:4 - diazaindene - 2)(1 - methyl - 2 - quinoline) methincyanine perchlorate.

A mixture of 1:1 - diethyl - 2 - methyl - 3:4 - diazaindene (0.70 g.), 2 - methylthioquinoline (0.70 g.) and methyl toluene - *p*-sulphonate (1.6 g.) was fused at 140° for  $1\frac{1}{2}$  hours, and then refluxed for 30 minutes with pyridine (5 ml.). Addition of an aqueous solution of sodium perchlorate precipitated the dye, which was obtained as yellow-brown plates, m. pt. 207—208°, by crystallisation from ethanol.

#### EXAMPLE 17.

(1:1:4:5 - Tetramethyl - 3:4 - diazaindene - 2)(3 - methyl - 2 - benzothiazole) methincyanine iodide.

A solution of 1:1:2:5 - tetramethyl - 3:4 - diazaindene - 4 - methiodide (1.58 g.) and 2-methylthiobenzothiazole methiodide (1.62 g.) in ethanol (20 ml.) was refluxed with triethylamine (1.0 ml.) for 30 minutes. The dye which separated was obtained as orange plates with a blue reflex, m. pt. 347—349° (decomp.), by crystallisation from a mixture of 2-methoxyethanol and methanol.

The dye extended the sensitivity of a silver chloride photographic emulsion to 5000 Å with a maximum at 4700 Å.

#### EXAMPLE 18.

(1:1:4:5 - Tetramethyl - 3:4 - diazaindene - 2)(3 - methyl - 2 - benzoxazole) trimethincyanine iodide.

A mixture of 1:1:2:5 - tetramethyl - 3:4 - diazaindene - 4 - methiodide (0.63 g.) and 2 -  $\omega$  - acetanilidovinylbenzoxazole methiodide (0.84 g.) was refluxed in pyridine (15 ml.) for 30 minutes. The dye which separated was recrystallised from 2-methoxyethanol, when it formed mauve needles, m. pt. 301—302° (decomp.).

The dye extended the sensitivity of a silver iodobromide photographic emulsion to 5800 Å with a maximum at 5650 Å.

## EXAMPLE 19.

(1:1:4:7 - Tetramethyl - 3:4 - diazaindene-2)(3 - methyl - 2 - benzoxazole) trimethincyanine iodide.

- 5 A solution of 1:1:2:7 - tetramethyl - 3:4 - diazaindene - 4 - methiodide (0.63 g.) and 2 -  $\omega$  - acetanilidovinylbenzoxazole methiodide (0.84 g.) in pyridine (5 ml.) was refluxed for 30 minutes, when the dye separated. It was  
10 obtained as mauve needles, m. pt. 283—284° (decomp.), by crystallisation from methanol.

The dye extends the sensitivity of a silver iodobromide photographic emulsion to 6050 Å with a maximum at 5600 Å.

## EXAMPLE 20.

(1:1:4:7 - Tetramethyl - 3:4 - diazaindene-2)(3 - methyl - 2 - benzothiazole) trimethincyanine iodide.

- 15 The method of Example 19 was used, and the dye was obtained as deep blue needles, m. pt. 271—272°, by crystallisation from methanol.

20 The dye extends the sensitivity of a silver iodobromide photographic emulsion to 6400 Å with maxima at 5650 and 6000 Å.

## EXAMPLE 21.

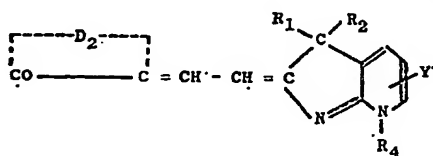
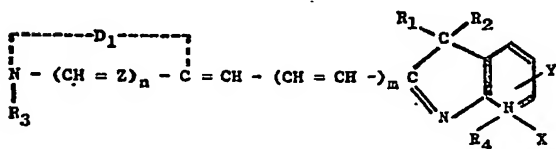
5 - (2:4 - Dihydro - 1:1:4:7 - tetramethyl-3:4 - diazaindenylidene - 2) - ethylidene-3 - ethyl - 2 - thiothiazolid - 4 - one.

- 30 A solution of 1:1:2:7 - tetramethyl - 3:4 - diazaindene - 4 - methiodide (0.64 g.) and 5-ethoxymethylene - 3 - ethyl - 2 - thiothiazolid-4-one (0.44 g.) in ethanol (10 ml.) was refluxed with triethylamine (0.5 ml.) for 30 minutes, when the dye separated from the solution. It  
35 was recrystallised from 2-methoxyethanol, and formed bronze plates, m. pt. 297—298° (decomp.).

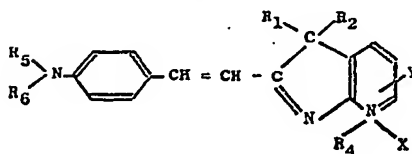
40 The dye extends the sensitivity of a silver iodobromide photographic emulsion to 6350 Å with maxima at 5600 and 6000 Å.

## WHAT WE CLAIM IS:—

1. A cyanine dye containing a diazaindene nucleus and being of the general formula:—



or

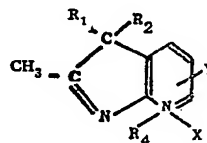


where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each a lower alkyl group,  $R_3$  is a lower alkyl or hydroxy-alkyl group or an aralkyl group,  $R_4$  is a lower alkyl or aralkyl group,  $n$  and  $m$  are each nought or one,  $X$  is an acid radicle,  $Y$  is hydrogen or a lower alkyl substituent group,  $Z$  is CH or N,  $D_1$  is the residue of a five-  
50 membered or six-membered heterocyclic nitrogen ring system, and  $D_2$  is the residue of a keto-methylene nucleus.

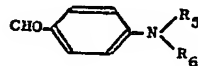
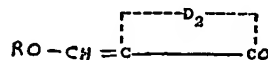
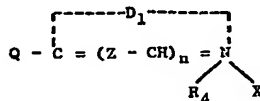
2. A cyanine dye according to claim 1  
60 wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  are methyl or ethyl groups.

3. A cyanine dye according to claim 1 as identified in any one of the foregoing specific  
65 Examples 1 to 21.

4. A process for the production of a cyanine  
dye as defined in claim 1 which comprises con-  
70 densing a compound of the general formula:—



with a compound of one of the formulae:—

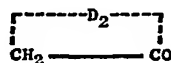


where  $Q$  is a thioether (SR), thioether vinyl ( $-\text{CH}=\text{SR}$ ) or acetanilidovinyl group,  $R$  is a lower alkyl group, and the other symbols  
75 have the meanings assigned to them in claim 1.

5. A process according to claim 4 wherein there is employed, instead of a compound of the first stated formula, a compound of the  
80 formula:—



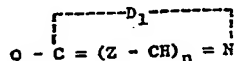
a compound of the formula: —



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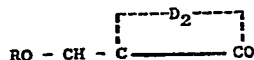
together with a substantially equimolecular proportion of a quaternising salt  $R_4X$ .

- 5 6. A process according to claim 5 wherein a compound of the formula set forth in claim 5, a compound of the formula: —



and at least two molecular proportions of an alkyl *p*-toluene sulphonate are employed.

- 10 7. A process according to claim 4 wherein there is used, instead of a compound of the formula: —



together with a substantially equimolecular proportion of a lower alkyl ortho ester.

8. A process according to any of claims 4—7 effected in the presence of a basic condensing agent.

9. A process for the production of a cyanine dye as defined in claim 1, substantially as set forth in any of the foregoing specific Examples 1 to 21.

10. A photographic silver halide emulsion containing, in sensitising amount, a cyanine dye as defined in any of claims 1—3.

20

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V. GALLAFENT,  
Chartered Patent Agent,  
23, Roden Street, Ilford, Essex.

## PROVISIONAL SPECIFICATION

### Improvements in or relating to Methine Dyes

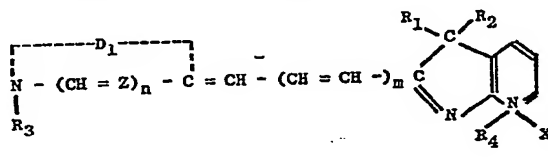
- 30 We, ILFORD LIMITED, of 23, Roden Street, Ilford, in the County of Essex, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to cyanine dyes and particularly to cyanine dyes which contain a 3:4-diazaindene ring system. The invention

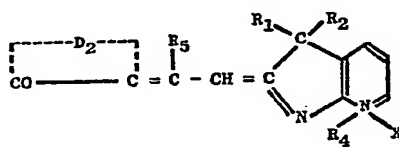
further relates to photographic silver halide emulsions containing such dyes as optical sensitisers.

According to the present invention there are provided cyanine dyes of the general formulae I, II and III:—

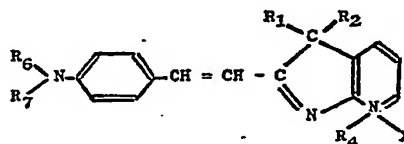
40



... I



... II



... III

- 45 where  $R_1$ ,  $R_2$ ,  $R_6$  and  $R_7$  are each a lower alkyl group,  $R_3$  is a lower alkyl or hydroxyalkyl group or an aralkyl group,  $R_4$  is a lower alkyl or aralkyl group and  $R_5$  is a hydrogen atom or a lower alkyl group,  $n$  and  $m$  are each nought or one,  $X$  is an acid radicle,  $Z$  is  $CH$  or  $N$ ,  $D_1$  is the residue of a five-membered or six-membered heterocyclic nitrogen ring

system, and  $D_2$  is the residue of a ketomethylene nucleus.

The substituents  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_6$  and  $R_7$  are preferably methyl or ethyl groups.  $R_5$  is preferably hydrogen.

$D_1$  may be the residue of any five-membered or six-membered heterocyclic ring system including thiazoles, oxazoles, selenazoles and

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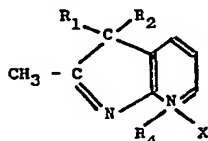


their polycyclic homologues such as those of the benzene and naphthalene series; pyridine and its polycyclic homologues, such as quinoline and  $\alpha$ - and  $\beta$ -naphthoquinolines; indolines; diazoles (e.g. 1:3:4 - thiadiazole); thiazolines; diazines (e.g. pyrimidines and quinazolines). The polycyclic compounds of these series may be substituted in the carbocyclic rings with one or more groups such as alkyl, aryl, alkoxy and methylene dioxy groups, or by halogen atoms.

$D_2$  may be the residue of rhodanic acid (2-thio - 4 - keto - tetrahydrothiazole), oxarhodanic acid (2 - thio - 4 - keto - tetrahydro-oxazole) and the N-hydrocarbon substituted derivatives of such compounds, oxazolones, pyrazole-5-ones and thiohydantoin.

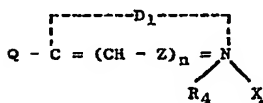
X may be any acid radicle, for example halide (chloride, bromide, iodide), sulphate, sulphamate, perchlorate or *p*-toluene sulphonate.

According to a further feature of this invention, compounds of the general formulae are prepared by condensing a compound of the general formula IV:—

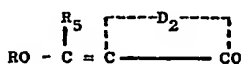


... IV

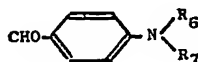
with a compound of one of the formulae V, VI and VII:—



... V



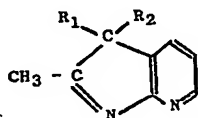
... VI



... VII

where Q is a thioether (SR), thioether vinyl ( $-\text{CH}=\text{CH}-\text{SR}$ ) or acetanilido vinyl group and R is a lower alkyl group.

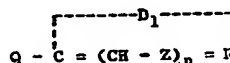
Instead of starting with a compound of general formula IV there may be used a compound of general formula IVa:—



... IVa

together with a substantially equimolecular proportion of a quaternising salt  $R_nX$ .

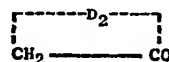
Further, when a quaternary salt such as the *p*-toluene sulphonate is used, the quaternisation may be effected by fusing an alkyl *p*-toluene sulphonate with the compound of formula IVa. The reaction may also be effected by starting with a compound of the formula IVa, a compound of the formula Va:—



... Va

and at least two molecular proportions of such a quaternising salt.

Further, there may be used, instead of a compound of formula VI a compound of formula VIa:—



... VIa

together with a substantially equimolecular proportion of a lower alkyl ortho ester.

Further, by using two molecular proportions of a compound of formula IV together with a molecular proportion of an alkyl orthoformate, symmetrical dyes containing two 3:4-diaza-indene nuclei are obtained.

All the foregoing condensations are facilitated by the presence of a basic condensing agent, e.g. pyridine or triethylamine.

The dyestuffs obtained, and particularly those of formula I, are valuable sensitizers for photographic gelatino silver halide emulsions and may be used for that purpose in the manner of sensitising dyes well known *per se*.

The following is illustrative of the production of suitable intermediates of Formula IV and IVa:—

1:1:2 - Trimethyl - 3:4 - diazaindene was prepared by the following procedure:—

2-Hydrazinopyridine (Fargher and Furness, *J.*, 1915, 107, 691) (115 g.), methyl isopropyl ketone (125 ml.) and dry benzene (300 ml.) were refluxed together, the water being removed as formed by azeotropic distillation. After distillation of the benzene, the residual oil was heated with zinc chloride (1 g.) at 250° until ammonia evolution ceased (2 hours). The product was distilled and the fraction boiling above 115°/6 mm. was collected and redistilled. The main fraction (b. pt. 109—132°/6 mm.) from the second distillation was extracted repeatedly with light petroleum (b. pt. 60—80°). The extracts deposited 1:1:2-trimethyl-3:4-diazaindene, which was obtained as colourless needles, m. pt. 77—78°, by repeated recrystallisations from cyclohexane.

1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide.

- 5 The base (2.0 g.), methyl iodide (2.0 ml.) and acetone (10 ml.) were refluxed together for 30 minutes, when the product separated from the solution. It was obtained as colourless needles, m. pt. 196—198° (decomp.) by crystallisation from ethanol.

- 10 Both the foregoing compounds of formula IV and the corresponding bases of formula IVa are novel *per se*, and they and their production form part of the present invention.

The following Examples will illustrate the present invention:—

15 EXAMPLE 1.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2) (3 - methyl - 2 - benzthiazole) methincyanine iodide.

- 20 1:1:2 - Trimethyl - 3:4 - diazaindene - 4-methiodide (1.52 g.) and 2 - methylthiobenzthiazole methiodide (1.62 g.) were refluxed together in spirit (30 ml.) containing triethylamine (1.0 ml.) for three hours. The dye separated from the solution on cooling, and was obtained as yellow plates, m. pt. 287—288° (decomp.) by recrystallisation from methanol.

- 25 The dye extends the sensitivity of a silver chloride photographic emulsion to 4950 Å with a maximum at 4700 Å.

EXAMPLE 2.

(4 - Ethyl - 1:1 - dimethyl - 3:4 - diazaindene - 2)(3 - ethyl - 2 - benzthiazole) methincyanine iodide.

- 35 The dye was prepared similarly to Example 1 and was obtained as yellow prisms with a blue reflex, m. pt. 300—302° (decomp.), by crystallisation from methanol.

- 40 The dye extends the sensitivity of a silver chloride photographic emulsion to 4950 Å with a maximum at 4700 Å.

EXAMPLE 3.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2) (1 - methyl - 2 - quinoline) methincyanine perchlorate.

- 45 The dye was prepared similarly to Example 1, was isolated by adding an aqueous solution of sodium perchlorate, and was obtained as red needles, m. pt. 242—244° (decomp.), by crystallisation from a mixture of 2-methoxy ethanol and methanol.

The dye extends the sensitivity of a silver chloride photographic emulsion to 5800 Å with a maximum at 5300 Å.

EXAMPLE 4.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2) (3 - methyl - 2 - benzoxazole) trimethincyanine iodide.

- 60 1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide (0.60 g.), 2 -  $\omega$  - acetanilidovinylbenzoxazole methiodide (0.84 g.) and pyridine

(5.0 ml.) were refluxed together for 15 minutes. The dye, which crystallised from the solution, was obtained as blue needles, m. pt. 258—259° (decomp.), by recrystallisation from a mixture of 2-methoxy ethanol and methanol.

The dye extends the sensitivity of a silver iodobromide photographic emulsion to 6000 Å with maxima at 5200 and 5600 Å.

EXAMPLE 5.

(1:1:4 - Trimethyl - 3:4 - diazaindene - 2) (1:3:3 - trimethyl - 2 - indolenine) trimethincyanine perchlorate.

The dye was prepared similarly to Example 4, was isolated by pouring the pyridine solution into an aqueous solution of sodium perchlorate, and was obtained as brown prisms with a blue reflex, m. pt. 238—240° (decomp.), by crystallisation from methanol.

The dye extends the sensitivity of a silver iodobromide photographic emulsion to 6250 Å with maxima at 5900 and 6200 Å.

EXAMPLE 6.

Bis - (1:1:4 - trimethyl - 3:4 - diazaindene - 2) trimethincyanine iodide.

1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide (0.76 g.), ethyl orthoformate (1.6 ml.) and pyridine (10 ml.) were refluxed together for 45 minutes. The dye crystallised out on cooling the solution, and was obtained as green plates, m. pt. 264° (decomp.), by recrystallisation from spirit.

The dye imparts a new band of sensitivity to a silver iodobromide photographic emulsion from 5900 to 6400 Å with a maximum at 6200 Å.

EXAMPLE 7.

4 - (2:4 - Dihydro - 1:1:4 - trimethyl - 3:4 - diazainden - 2 - ylidene) - ethylidene - 3-methyl - 1 - phenylpyrazol - 5 - one.

Ethyl orthoformate (1.6 ml.) was added to a boiling solution of 1:1:2 - trimethyl - 3:4 - diazaindene 4-methiodide (0.76 g.) and 3-methyl - 1 - phenylpyrazol - 5 - one (0.71 g.) in pyridine (5 ml.), and the whole refluxed for 30 minutes. The dye, which crystallised out on cooling, was recrystallised from spirit as red plates and needles, m. pt. 239—241° (decomp.).

The dye imparts a new band of sensitivity to a silver chloride photographic emulsion from 4600 to 5550 Å with a maximum at 5350 Å.

EXAMPLE 8.

5 - (2:4 - Dihydro - 1:1:4 - trimethyl - 3:4 - diazainden - 2 - ylidene) - ethylidene - 3-ethyl - 2 - thiothiazolid - 4 - one.

1:1:2 - Trimethyl - 3:4 - diazaindene 4-methiodide (0.76 g.) and 5-ethoxymethylene-3 - ethyl - 2 - thio - thiazolid - 4 - one (0.54 g.) were refluxed in spirit (10 ml.) and triethylamine (1.0 ml.) for 20 minutes. The precipitated dye was obtained as purple plates,

m. pt. 247—249° (decomp.), by crystallisation from a mixture of 2-methoxy ethanol and methanol.

- 5 The dye extends the sensitivity of a silver iodobromide emulsion to 6300 Å with a maximum at 6000 Å.

EXAMPLE 9.

- 2 - [2 - (*p* - dimethylaminophenyl) - vinyl] -  
1:1 - dimethyl - 3:4 - diazaindene 4-  
10 methiodide.  
1:1:2 - Trimethyl - 3:4 - diazaindene-  
4-methiodide (0.60 g.) and *p*-dimethylamino-  
benzaldehyde (0.30 g.) were refluxed in pyri-

dine (5 ml.) containing piperidine (1 drop) for 1½ hours. The dye which crystallised out on cooling was obtained as green needles, m. pt. 259—260° (decomp.), by recrystallisation from methanol. 15

The dye extends the sensitivity of a silver iodobromide emulsion to 6200 Å. 20

V. GALLAFENT,  
Chartered Patent Agent,  
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